

Near-field spectroscopy and photochemistry from first principles beyond the dipole approximation

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Optical near field refers to a non-propagating light field localized around an emitter or scatterer such as metallic nanostructures. The interaction between the near-field and molecules can overcome the diffraction limit of a propagating light, induce non-dipolar excitations, and enable nanoscale chemical analysis down to single molecule even with sub-molecular resolutions. Recent experiments utilizing scanning tunneling microscopy offer a unique platform for nanoscale spectroscopy and microscopy [1], as well as photochemistry [2]. From the theoretical perspective, the optical near-field excitation of molecules requires us to go beyond the dipole approximation, which is not possible with available *ab initio* codes. In this paper, a first principles method based on the multipolar Hamiltonian for electronic and vibrational excitations and their applications to near-field IR and Raman spectroscopies will be described [3-7]. In addition, some of our theoretical efforts on near-field photochemistry will be given [8].

- [1] R. B. Jaculbia, T. Iwasa et al., *Nat. Nanotechnol.* 15, 105 (2020).
- [2] E. Kazuma et al., *Science*, 360, 521 (2018).
- [3] T. Iwasa and K. Nobusada, *Phys. Rev. A*, 80, 043409 (2009).
- [4] T. Iwasa and K. Nobusada, *Phys. Rev. A*, 82, 043411 (2010).
- [5] T. Iwasa, M. Takenaka, T. Taketsugu, *J. Chem. Phys.*, 144, 124116 (2016).
- [6] M. Takenaka, T. Taketsugu, T. Iwasa, *J. Chem. Phys.*, 152, 164103 (2020).
- [7] M. Takenaka, T. Taketsugu, T. Iwasa, *J. Chem. Phys.*, 154, 024104 (2021).
- [8] K. Toda, Y. Hirose, E. Kazuma, Y. Kim, T. Taketsugu, T. Iwasa*, *J. Phys. Chem. A*, 126, 4191-4198 (2022).